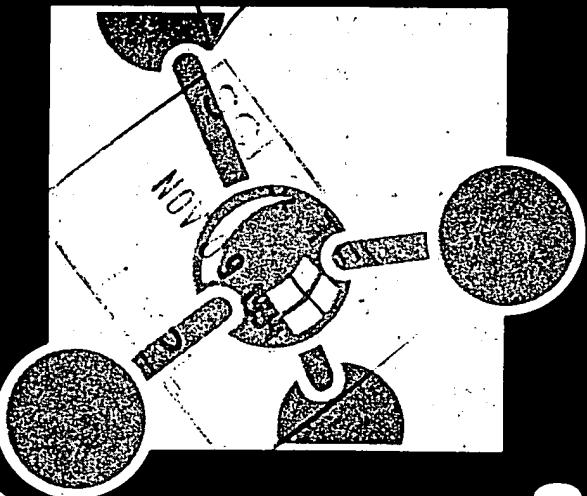


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## Mechanism of the Gibbs Reaction. 3.<sup>1</sup> Indophenol Formation via Radical Electrophilic Aromatic Substitution (S<sub>REAr</sub>) on Phenols

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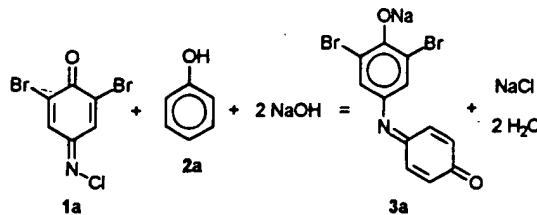
Different products are formed, depending on the *para* substituent (R) when 2,6-dichlorobenzoquinone *N*-chloroimine (**1b**) reacts with the anion of the 4-substituted phenol (**2**). If the group R can leave as a cation (i.e., R is an electrofugal leaving group) such as H, CH<sub>2</sub>NMe<sub>2</sub>, CH<sub>2</sub>OH, etc., then the reaction yields indophenol (**3**), the normal Gibbs product. If the group R cannot leave as a cation such as CH<sub>3</sub>, the final product of the reaction will be type **10**, 1,1-disubstituted 2,5-cyclohexadienone. If the group R is OH or NH<sub>2</sub>, then the reaction gives the corresponding benzoquinone **4** or benzoquinone imine **1** and 2,6-dichlorobenzoquinone imine (**1d**). In all these cases the reaction proceeds at a 1:1 stoichiometry. If, however, the group R can leave as an anion (i.e., R is a nucleofugal leaving group) such as halogen, alkoxy, or OCH<sub>2</sub>Ph, then the reaction proceeds at a 1:2 stoichiometry. In this case the reaction of a second mole of phenolate with type **26** intermediate yields the indophenol product **3** and the oxidized product of the phenol. If the two *ortho* positions of the phenolate are substituted then the oxidized product of the phenol will be the corresponding benzoquinone. The mechanism of the reaction has been studied by kinetic and nonkinetic (NMR) methods. It has been concluded that the first step of the mechanism is a single electron transfer (SET) from the phenolate to the benzoquinone *N*-chloroimine **1b** which is the rate-determining process in most of the cases. In some of the nucleofugal cases the final oxidation, involving the second mole of phenolate, is the rate-determining step. For the radical reaction three different alternatives are suggested: a combination of radicals in a solvent cage (direct reaction) and two different chain reactions (chain A and chain B). Quantum chemical calculations revealed that the direct reaction and the chain A mechanisms were energetically more favored than chain B. The reaction shows an extremely large *para* selectivity although the substitution does follow a radical mechanism.

### Introduction

In 1927 H. D. Gibbs suggested the use of 2,6-dibromobenzoquinone *N*-chloroimine (**1a**) as a phenol assay reagent<sup>2</sup> (Scheme 1). According to his method, phenol (**2a**) reacts quantitatively with **1a** in alkaline solution to give the blue<sup>3,4</sup> anion of indophenol **3a**, the concentration of which is established by colorimetric methods.

Since then the Gibbs reaction has been generally used,<sup>5-19</sup> but **1a**<sup>5-8</sup> is replaced in most cases by the cor-

Scheme 1



responding 2,6-dichloro compound **1b**.<sup>8-15</sup> The assay is usually positive even in the case when the phenol measured carries a substituent other than hydrogen at the *para* position, e.g., CH<sub>2</sub>NH<sub>2</sub>,<sup>6</sup> CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>,<sup>6</sup> CH<sub>2</sub>OH,<sup>17</sup> COOH,<sup>18</sup> OCH<sub>2</sub>Ph,<sup>6</sup> alkoxy,<sup>6,10-12</sup> Cl,<sup>6,10</sup> Br,<sup>10</sup> and I,<sup>10,12</sup> or even F.<sup>12</sup> It is remarkable that among these *para* substituents there are several which can be eliminated exclusively as a nucleofugal leaving group.

A mechanism of this reaction was suggested by D. Svobodova et al.<sup>8</sup> as well as by P. D. Josephy and A. van Damme.<sup>12</sup> Accordingly, in an alkaline solution, **1a** or **1b** is converted into 2,6-dihalobenzoquinone imine **1c** or **1d** and hypochlorite, where the former are the active reagents being responsible for the reaction. This hypothesis seems to be rather convincing since it is well known that **1d** and its analogues give indophenol **3** with phenol if it is replaced with nucleofugal leaving groups at C-4.<sup>20-23</sup>

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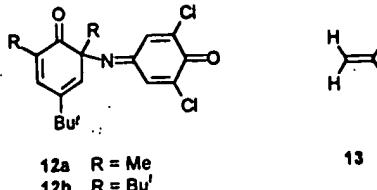
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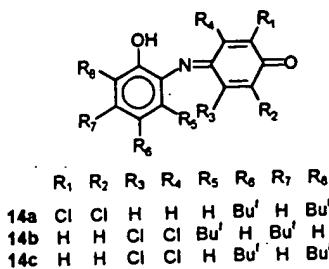
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(13). In these experiments due to the steric hindrance of the 4-*tert*-butyl group along with compounds type 10, type 3 indophenols and *ortho*-substituted derivatives could also be isolated. Accordingly, in the reaction of 4-*tert*-butylphenol (2r) with 1b besides indophenol 3f, tricyclic compounds 11a and 11d were formed, too. Similarly 2,6-dimethyl-4-*tert*-butylphenol (2s) gave 3b and 1,1-disubstituted 2,4-cyclohexadienone 12a. In the



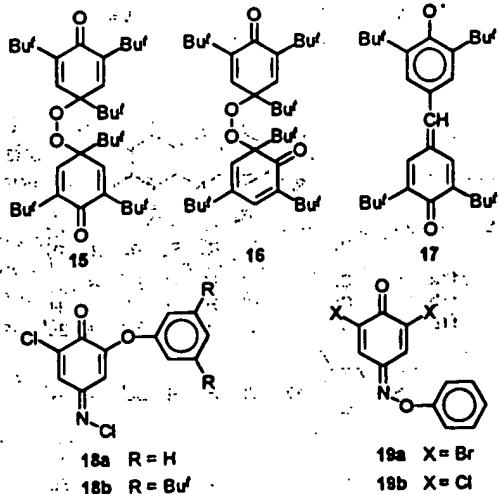
12a R = Me  
12b R = Bu'

13



14a Cl Cl H H H H Bu' H Bu'  
14b H H Cl Cl Bu' H Bu' H  
14c H H Cl Cl H Bu' H Bu'

reaction of these phenols (2r and 2s), the type 10 intermediates, leading to indophenols 3f and 3b, respectively, could not be observed. However, during the reaction of 2,4,6-tri-*tert*-butylphenol (2q), both the intermediates 10i (*para*) and 12b (*ortho*), respectively, were formed, and in the case of 12b even its transformation into *o*-indophenol 14a and then cyclization into 11c could be detected by <sup>1</sup>H-NMR in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> (TCE). Attempts to isolate 14a failed, since during preparative thin layer chromatography (prep TLC), 14a cyclized into the tricyclic 11c. In the Gibbs reaction of phenol 2q, peroxides 15 and 16 were also formed due to trapping of the 2,4,6-tri-*tert*-butylphenoxy radical<sup>31</sup> by an oxygen molecule.<sup>32</sup> Formation of peroxides 15 and 16 raises the question whether the homolytic reaction occurs only in the case of 2q or the Gibbs reaction itself is homolytic in general. We found that the formation of the parent indophenol 3h from 2a and 1e could be inhibited<sup>33</sup>



18a R = H  
18b R = Bu'

19a X = Br  
19b X = Cl

using radical scavengers such as 2,6-dichloronitrosobenzene (DCNB), 2,2,6,6-tetramethylpyridine-*N*-oxyl (TEMPO) or galvinoxyl (17). The effect of these scavengers clearly demonstrates that the indophenol formation

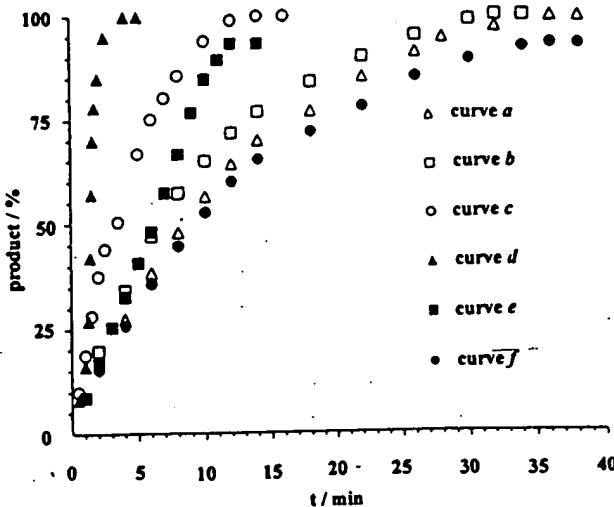


Figure 1. The acceleration effect of acetonitrile on the Gibbs reaction of 1b with 2a and the blocking effect of TEMPO on this acceleration, in borate buffer (pH = 9.2) at 295 K with  $[1b] = 6.14 \times 10^{-5}$  mol dm<sup>-3</sup> and  $[2a] = 2.98 \times 10^{-3}$  mol dm<sup>-3</sup>, where product vs time is plotted. ( $\Delta$ )  $[MeCN] = 0.15$  vol %, ( $\square$ )  $[MeCN] = 2.65$  vol %, ( $\circ$ )  $[MeCN] = 4.65$  vol %, ( $\blacktriangle$ )  $[MeCN] = 10.15$  vol %, ( $\blacksquare$ )  $[MeCN] = 10.15$  vol % and  $[TEMPO] = 1.23 \times 10^{-5}$  mol dm<sup>-3</sup>, ( $\bullet$ )  $[MeCN] = 10.15$  vol % and  $[TEMPO] = 3.68 \times 10^{-5}$  mol dm<sup>-3</sup> or  $2.45 \times 10^{-4}$  mol dm<sup>-3</sup>.

from 2a and 1e is a radical reaction, and a consecutive ionic mechanism can be excluded.<sup>34</sup> Furthermore, although radicals could not be detected by ESR study, the fast consumption of the added radical scavenger TEMPO indicated indirectly a radical reaction. Interestingly, the kinetics of the Gibbs reaction of 2a and 1b were not affected by scavengers. However, the addition of some acetonitrile to the solvent had a dramatic effect on this reaction.<sup>35</sup> In Figure 1 the dependence of the product vs time curve with increasing acetonitrile concentration is depicted (curves a-d). Even 10% of acetonitrile<sup>36</sup> changed the second-order curve to an S-shaped one with a considerable acceleration (curve d). Even more interesting is that the effect of acetonitrile could be blocked by TEMPO (curves e, f), and applying more than 0.6 1b equiv of TEMPO, curve a could be recovered.<sup>37</sup> These results suggest that the Gibbs reaction of 2a and 1e is a radical chain reaction since it can be inhibited by scavengers, but that of 2a and 1b is not. Furthermore, in the presence of acetonitrile, a radical direct and a

(29) This indophenol is a 2:1 mixture of the two tautomers 3fa and 3fb in chloroform-*d*.

(30) Further oxidation of the dimer 7b indicates that when there is not sufficient phenol to be oxidized, the dimers take part in the reaction. Indeed, applying an excess of 1b (1:4), several unidentified polymers formed, rather than the dimers as phenol oxidation products. In those reactions, when the oxidation of the phenol afforded the corresponding quinone, this latter always formed, independently whether the phenol, or 1b was in excess.

(31) Cook, C. D.; Woodworth, R. C. *J. Am. Chem. Soc.* 1953, 75, 6242-6244.

(32) When the reaction is carried out under argon atmosphere, only 10i and 12b formed.

(33) The indophenol formation could be prevented with DCNB and TEMPO, but could not with galvinoxyl, because of its low solubility to reach this stage.

(34) Zhang, X.-M.; Yang, D.-L.; Liu, Y.-C. *J. Org. Chem.* 1993, 58, 224-227.

(35) Moderate acceleration has been also observed in the presence of 10% of DMSO or *tert*-butyl alcohol, but their effect could not be offset by TEMPO (the second-order kinetic remained in these solvents).

(36) Propionitrile has the same effect.

(37) In the presence of 10% of acetonitrile 30% hyperchromic effect was observed on the UV spectra of indophenol 3f. DMSO and *tert*-butyl alcohol did not show this effect.

Table 4. Effect of Metal Ions on the Kinetics of the Gibbs Reaction of 2a with 1b<sup>a</sup>

metal ion	concentration $\times 10^{-5}$ mol dm <sup>-3</sup>	$t_{1/2}$ , s
$Mn^{2+}$	2.45	50
	6.13	40
	12.10	38
	30.70	110
$Ag^+$	61.30	95
	92.00	95
$Cu^{2+}$	6.13	200
	24.60	200
none		480

<sup>a</sup> 1b ( $6.13 \times 10^{-5}$  mol dm<sup>-3</sup>) and 2a ( $2.93 \times 10^{-3}$  mol dm<sup>-3</sup>) in borate buffer (pH = 9.2) at 22 °C.

radical chain reaction proceeds simultaneously, since the radicals, having escaped from the reaction cage by the assistance of acetonitrile, could start a parallel chain reaction,<sup>38</sup> the chain carriers of which could be scavenged again.

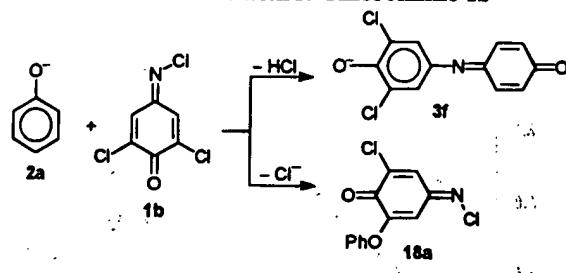
Similarly to acetonitrile,  $Mn^{2+}$  had the same dramatic effect which could be blocked by TEMPO.  $Ag^+$  and  $Cu^{2+}$  showed similar but less pronounced effects (Table 4). However, these ions, similarly to acetonitrile, did not affect the reaction of 2a and 1e. These results suggest that these ions facilitate merely the electron transfer from phenolate 2a to *N*-chloroimine 1b, but do not afford further chain initiators (over the ones escaped from the solvent cage) with either reactant alone.<sup>39</sup>

**Reactions in Nonaqueous Medium.** The reaction of the sodium salt of 2a and 1b in several dipolar aprotic and apolar aprotic solvents, monitored by <sup>1</sup>H-NMR, was very fast compared to that in aqueous solution (pH = 9.2). In dipolar aprotic solvents, e.g., in DMSO-*d*<sub>6</sub>, DMF-*d*<sub>7</sub>, and acetonitrile-*d*<sub>3</sub>, the main product was the phenol ether 18a, the carbon-substituted product, whereas in apolar aprotic solvents, e.g., in pyridine-*d*<sub>5</sub>, chloroform-*d*, benzene-*d*<sub>6</sub>, and carbon tetrachloride, indophenol 3f was formed, similarly to the aqueous medium, along with traces of 18a (Table 5).<sup>40</sup> The formation of 3f both in water as well as in apolar aprotic solvents, despite the difference between their dielectric constants, i.e., their polarity, is probably due to the fact that, in both types of solvent the oxygen atom of the phenolate anion is blocked either by solvation with a hydrogen bond in water or by ion aggregation in apolar aprotic solvents. When tetraethylammonium phenolate was used instead of the sodium salt in chloroform-*d* as solvent, the amount of 18a increased considerably, demonstrating the higher reactivity of the phenolate oxygen when a softer and bulkier cation, forming a less compact aggregate, was applied. In dipolar aprotic solvents when only the cation is solvated, the naked phenolate anion is extremely active at the oxygen site, which explains the formation of 18a. This hypothesis was backed by the fact that unlike the sodium salt of 3,5-di-*tert*-butylphenol (2t), which does not react in aqueous solution with 1b and forms phenol ether

(38) The hyperchromic effect of acetonitrile on the UV spectra of the indophenol 3f indicates a characteristic solvating effect on the product 3f. On this base, a similar solvent effect might be supposed during the reaction, i.e., on the chain initiation.

(39) We think that the acceleration effect of these metal ions is that they assist the electron transfer from increased distance, making possible the escape of chain initiators from the cage by solvation, and start a chain reaction, being concurrent with the in-cage direct reaction.

(40) In 18a the *anti*-arrangement of the *N*-chloro atom was determined by the assignment of the analogous 1b: Saito, H.; Nukada, K. *J. Can. Chem.* 1968, 46, 2989–3000.

Table 5. Solvent Dependence of the Gibbs Reaction of Phenolate 2a with *N*-Chloroimine 1b

solvent	$\epsilon_{25}^{\circ}\text{C}$	18a, %	3f, %
water	78	<1	>99
DMSO- <i>d</i> <sub>6</sub> + 27% D <sub>2</sub> O	38	62	
DMSO- <i>d</i> <sub>6</sub> + 11% D <sub>2</sub> O	85	15	
DMSO- <i>d</i> <sub>6</sub>	46.6	96	4
DMF- <i>d</i> <sub>7</sub>	37.0	97	3
acetonitrile- <i>d</i> <sub>3</sub>	36.2	87	13
pyridine- <i>d</i> <sub>5</sub>	12.3	20	80
chloroform- <i>d</i> <sup>a</sup>	4.6	<1	>99
chloroform- <i>d</i> /pyridine- <i>d</i> <sub>5</sub> 9/1	<1	<1	>99
chloroform- <i>d</i> <sup>b</sup>	24	76	
benzene- <i>d</i> <sub>6</sub> <sup>a</sup>	2.3	2	98
carbon tetrachloride <sup>a</sup>	2.2	25	75

<sup>a</sup> Sodium phenolate dissolved by 18-crown-6. <sup>b</sup> Tetraethylammonium phenolate applied instead of sodium phenolate.

18b in DMSO-*d*<sub>6</sub> immediately, the sodium salt of 2,6-di-*tert*-butylphenol (2u) forms indophenol 3e with 1b in both solvents.

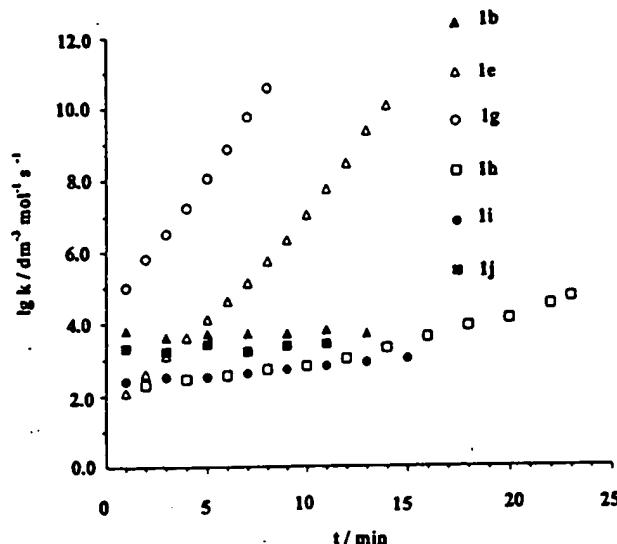
**Mechanistic Considerations.** In his pioneering paper, Gibbs<sup>2</sup> suggested that the most likely nucleophilic centrum would be the negatively charged phenolic oxygen in the reaction of *N*-chloroimine 1a. Accordingly, an intermediate aryl oxime ether 19a should be formed, the rearrangement of which into the indophenol is fast; therefore, it would not influence the reaction rate. Checking this hypothesis, the dichloro derivative 19b was synthesized. However, under the conditions of the Gibbs reaction, aryl oxime ether 19b remained unchanged excluding it as a possible intermediate.<sup>41</sup> The reactions of 1b with phenol 2u or with its 4-amino derivative 2v were very fast (in the latter case 1d and 1f were formed), but there was no reaction between phenol 2t and 1b or 1d. Accordingly, any mechanism giving priority to the attack of the phenolic oxygen can be excluded. We suggest that the nitrogen atom of 1b attacks the *para* position of the phenol directly.<sup>42</sup> Although the prevention of the *para* substitution of phenol 2t with *N*-chloroimine 1b can also be rationalized by steric hindrance, that of the *ortho* substitution hardly can.<sup>43</sup>

According to Gibbs,<sup>2</sup> the rate of the formation of indophenol 3a depends on the pH, but it does not when the phenolate anion ( $PhO^-$ ) is considered as a reactive partner. Our experiments were in full agreement with this statement in the case of phenol 2a, as the rate constant  $v = k[1b][PhO^-]$  did not change when the molar

(41) Nevertheless, it should be noted that 19b could rearrange by a photochemical reaction into indophenol 3f and tricyclic 11b. As Gibbs reaction of 2a with 1b is not influenced by light and does not afford tricyclic product deriving from *o*-indophenol, this hypothesis can be rejected.

(42) The fact that *ortho*-substituted derivatives are also formed from 4-*tert*-butylphenols is due to the steric hindrance of the *tert*-butyl group.

(43) There is some evidence that the chloro and hydrogen substitutions on benzoquinone *N*-chloroimines have a special effect on the regioselectivity, since 3,5-dichloro 1g did afford *ortho* products with 2t. Accordingly, in the reaction of 2t and 1g, the two tricyclic isomers 11e and 11f were formed via interconversion of the *o*-indophenol intermediates 14b, c.

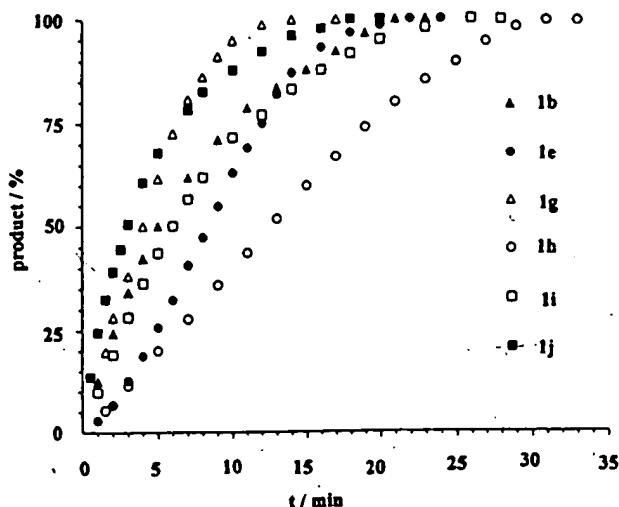


**Figure 2.** Hypothetical second-order rate constants vs time plot of the Gibbs reaction of several benzoquinone *N*-chloroimines with 2a in borate buffer (pH = 9.2) at 295 K where the concentration of benzoquinone *N*-chloroimines was always  $6.14 \times 10^{-5}$  mol dm $^{-3}$  and  $f$  = the rate of the observed and depicted  $k$ . ( $\blacktriangle$ ) [2a] =  $4.88 \times 10^{-3}$  mol dm $^{-3}$ ,  $f = 1$ ; ( $\triangle$ ) [2a] =  $2.36 \times 10^{-1}$  mol dm $^{-3}$ ,  $f = 10^{-2}$ ; ( $\circ$ ) [2a] =  $2.93 \times 10^{-3}$  mol dm $^{-3}$ ,  $f = 1$ ; ( $\square$ ) [2a] =  $2.28 \times 10^{-2}$  mol dm $^{-3}$ ,  $f = 10^{-1}$ ; ( $\bullet$ ) [2a] =  $5.86 \times 10^{-3}$  mol dm $^{-3}$ ,  $f = 1$ ; ( $\blacksquare$ ) [2a] =  $7.6 \times 10^{-4}$  mol dm $^{-3}$ ,  $f = 10$ .

concentration of *N*-chloroimine 1b and that of  $\text{PhO}^-$  was commensurable, independently of the molar ratio of 2a and 1b which could be in the range of 30–530:1. Investigating the kinetics of 2a with other benzoquinone *N*-chloroimine derivatives 1e and 1g–j, we have concluded that the occurrence of the second-order kinetics depends on the reactivity of the benzoquinone *N*-chloroimine derivatives. The validity of the equation applied to calculate the second-order rate constants can be judged from the agreement of these points with the theoretical horizontal straight lines in Figure 2 where the hypothetical second-order rate constants of the reaction of 2a with several *N*-chloroimines type 1 vs time is plotted. Thus, the second-order rate can be applied on the reactions of 2a with 1b and 1j whereas it cannot on that with the parent 1e, the monochloro 1h, and the dichloro 1g and 1i.<sup>44</sup> Moreover, when the formation of indophenols are plotted against time (Figure 3) *N*-chloroimines 1b, 1i, and 1j give characteristic curves, while the less active 1e and 1h as well as 1g, being more active than 1b, deviate from these. The curve of parent *N*-chloroimine 1e shows well that the formation of the parent indophenol 3h is slow at the beginning of the reaction and then it accelerates, due to the chain reaction character proved previously.

To summarize these results, a collection of mechanisms shown in Schemes 4–6, is proposed for the Gibbs reaction of phenol 2a with *N*-chloroimines 1b or 1e. These *N*-chloroimines are typical representatives of the non-chain and the chain reaction mechanisms, respectively. These schemes demonstrate these two types of mechanisms and the connection between them.

The first step of the reaction is a reversible single electron transfer (SET) from phenolate 2a to *N*-chloroimine 1b or 1e forming a radical pair (20a and 21a or



**Figure 3.** Product vs time plot of the data depicted in Figure 2.

21b) in a solvent cage (Scheme 4). The formation and further transformation of this radical pair will influence the overall rate of the reaction. In the case of the more reactive 1b, the fast combination of 20a and 21a gives 22a and subsequent fast<sup>45</sup> elimination of hydrochloric acid yields indophenolate 3f.<sup>46</sup> Since both the combination and HCl elimination are fast, the oxidation of phenolate by SET remains the rate-determining step. Indeed, the second-order kinetics as well as the linear relationship of the logarithm of this second-order rate constant of the Gibbs reaction of 1b vs the half-wave oxidative potential of the reacting phenols (Figure 4) verify this theory.<sup>47</sup> When the less reactive 1e is the electron acceptor, the combination of 20a and 21b is negligible; therefore, the radicals, once escaped from the solvent cage, can start a chain reaction, which can be stopped completely by TEMPO. However, when the kinetics of the reaction of 1e and the more reactive phenols 2b or 2u were investigated, a second-order kinetics was obtained again, and the reaction could not be scavenged by TEMPO. Thus, the forward direction of the reaction toward combination, i.e., the combination of the radicals in the solvent cage (direct reaction) or the chain reaction via competitive escape of the radicals from the cage depends on the reactivity of the radicals forming the radical pair. Moreover, further connection between the nonchain and the chain reaction was demonstrated by the effect of acetonitrile or metal ions, as additives. These additives changed the mechanism from the former to the latter, as described above in the case of the reactions involving 1b. The radicals once escaped can enter into two alternative chains. In chain A (Scheme 5), the addition of phenoxy radical 20a to *N*-chloroimine 1e forms the radical adduct 23b, another SET to which

(45) Applying 4-deuteriophenol, a kinetic isotope effect was not observed.

(46) With radical 21a the loss of chloride ion in the solvent cage is an alternative possibility, followed by the combination of radicals 20a and 24a to give 28a. In the thermodynamic sense this process is not likely (see Table 8; cp. chain b), but a significantly exothermic solvation of the chloride ion can make the process possible.

(47) Above was shown, while *N*-chloroimines 1b and 1j gave a unchanged second-order rate constant with phenol in function of time (direct reaction in the solvent cage), the compounds 1e, 1g, 1h, and 1i gave growing rate constants proceeding with the reaction (chain reaction); therefore, only a qualitative relationship can be established between the reducibility of *N*-chloroimines and the logarithms of the rate constants.

(44) However, the reaction of 1e with more reactive phenols 2b and 2u shows second-order kinetics (see later).

Scheme 4

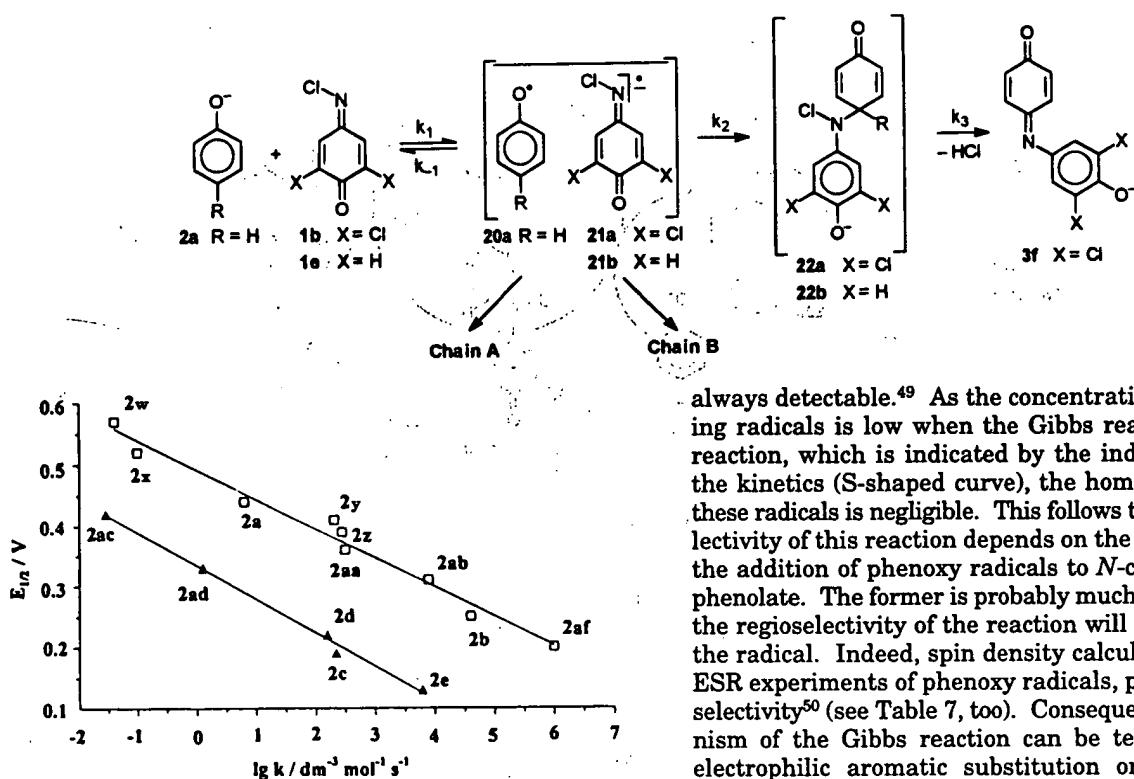


Figure 4. The plot of the oxidative  $E_{1/2}$  of several phenols vs the logarithm of the second-order rate constant of the Gibbs reaction of **1b** with these phenols in borate buffer (pH = 9.2) at 295 K.

from phenolate **2a** gives the same type of intermediate **22b** as in the direct reaction with a simultaneous recovery of the phenoxy radical **20a** to complete the chain. Fast dehydrochlorination of **22b**, similarly to that in the direct reaction in Scheme 4, affords the indophenolate **3h**. Consequently, considering the mechanism of chain A, it has the same intermediate **22** as the direct reaction, but the formation of this product is autocatalyzed by phenoxy radicals. In chain B (Scheme 6), a chloride elimination from radical anion **21b** gives imine radical **24b**, the addition of which to phenolate **2a** leads to the radical anion adduct **25b**. To complete the chain, a second SET is accomplished from adduct **25b** to *N*-chloroimine **1e** to recover radical anion **21b** with simultaneous formation of intermediate **26b**, the aromatization of which affords indophenolate **3h**. In this case the formed intermediate **26b** is different from that in chain A since the *N*-chloride has been eliminated already within the chain. Thus in the direct reaction and in chain A, the chloride ion and the proton can be eliminated simultaneously after the addition. This is an essential difference between the first two mechanisms and the third one, in which the chloride ion is eliminated early in the chain and the deprotonation occurs only in the terminating step.

On the other hand, the astonishing high regio- and chemoselectivity of the Gibbs reaction<sup>48</sup> raises other questions. In the reactions of phenolates involving phenoxy radicals, the dimerization or polymerization of the substrate affording a large variety of products are

(48) Monitoring the Gibbs reaction of *N*-chloroimines **1b** or **1e** with phenol **2a** by <sup>1</sup>H NMR in D<sub>2</sub>O, quantitative formation of indophenols **3f** or **3h** was observed.

always detectable.<sup>49</sup> As the concentration of the initiating radicals is low when the Gibbs reaction is a chain reaction, which is indicated by the inductive period in the kinetics (S-shaped curve), the homodimerization of these radicals is negligible. This follows that the chemoselectivity of this reaction depends on the reaction rates of the addition of phenoxy radicals to *N*-chloroimine or to phenolate. The former is probably much faster, therefore the regioselectivity of the reaction will be influenced by the radical. Indeed, spin density calculations, based on ESR experiments of phenoxy radicals, predict high *para* selectivity<sup>50</sup> (see Table 7, too). Consequently, any mechanism of the Gibbs reaction can be termed as radical electrophilic aromatic substitution or simply S<sub>REAr</sub>. Since both the initiating SET and the combination or the chain reaction is independent on the character of the *para* leaving group, this mechanism can be extended over all phenols reacting with benzoquinone *N*-chloroimines at the aromatic ring. Indeed, a similar straight line was obtained for 4-chlorophenols as for 4-unsubstituted phenols when the logarithm of the second-order rate constant vs  $E_{1/2}$  was plotted in Figure 4, and even the scavenger effect could be demonstrated in the reaction of *N*-chloroimine **1e** and phenols **2g**, **2f**, and **2ah** with DCNB. This generalization leads to type **22** intermediate adduct (Schemes 4, 5), further transformation of which depends on the leaving character of the *para* substituent (R). When R represents an electrofugal leaving group, e.g., CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> or *tert*-butyl, it transforms into type **3** indophenol with elimination of chloride anion and R<sup>+</sup>, as described above in the case of R = H. When R has a poor leaving character, after elimination of chloride anion from type **22** adduct, the formed bis-quinoidal compound either remains unchanged, e.g., when R = methyl to afford **10d-h** or, when R = OH, e.g., from hydroquinone (**2ai**) or 2,6-di-*tert*-butyl-4-hydroxyphenol (**2aj**), and NH<sub>2</sub>, e.g., from phenol **2v** or 2,6-dichloro-4-aminophenol (**2ak**), it decomposes to afford oxidized products of the phenol, e.g., quinones **4e** or **4d** and imines **1f** or **1d**, respectively, along with imine **1d** deriving from the reduction of *N*-chloroimine **1b** (**22c** in Scheme 7).

When R represents a nucleofugal leaving group, the further transformation of the type **22** intermediate adduct is demonstrated on the adduct of phenol **2c** and *N*-chloroimine **1b** (**22c** in Scheme 7).

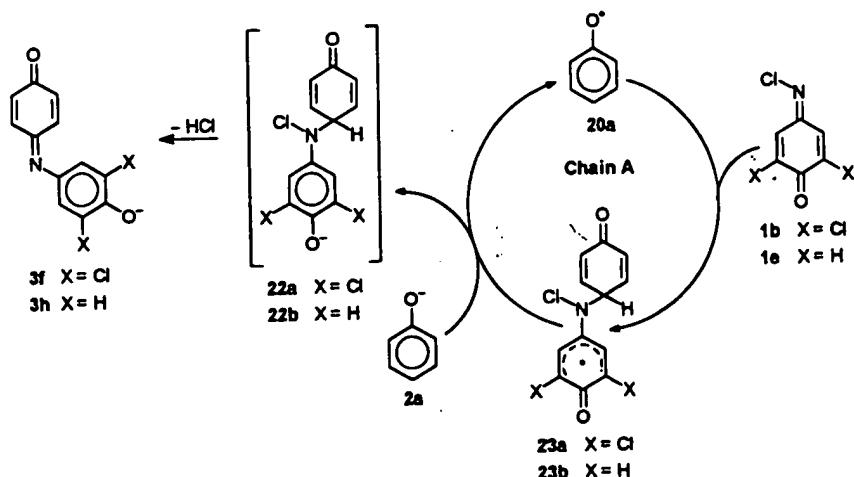
(49) Patai, S. *The Chemistry of the Hydroxyl Group*; John Wiley & Sons: New York, 1971; Part 1, pp 505–592.

(50) (a) Stone, T. J.; Waters, W. A. *J. Chem. Soc.* 1964, 213–218.

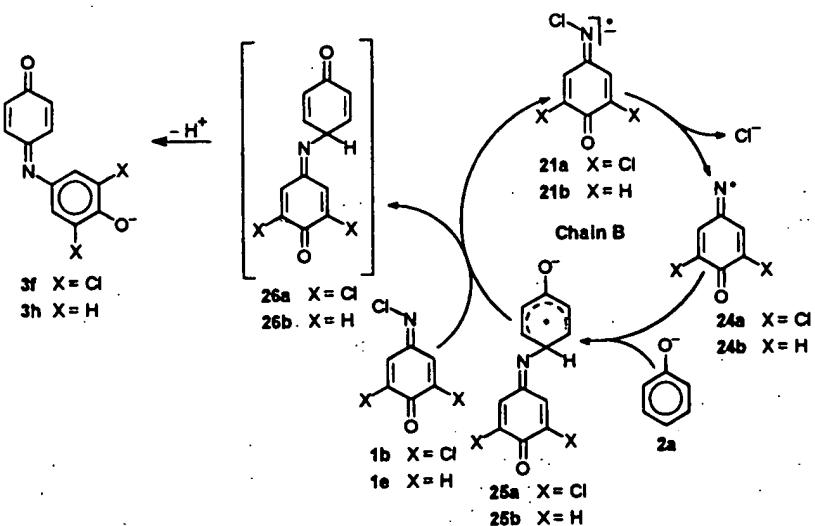
(b) Dixon, W. T.; Norman, R. O. *C. J. Chem. Soc.* 1964, 4857–4860.

(c) Potassium nitrosodisulfonate, ON(SO<sub>3</sub>K)<sub>2</sub>, known as Fermi's salt, affords preferentially *p*-quinones with *para*-unsubstituted phenols even when the *ortho* positions are free. This reaction is passing through a phenoxy radical intermediate (see ref 49, pp 568–569).

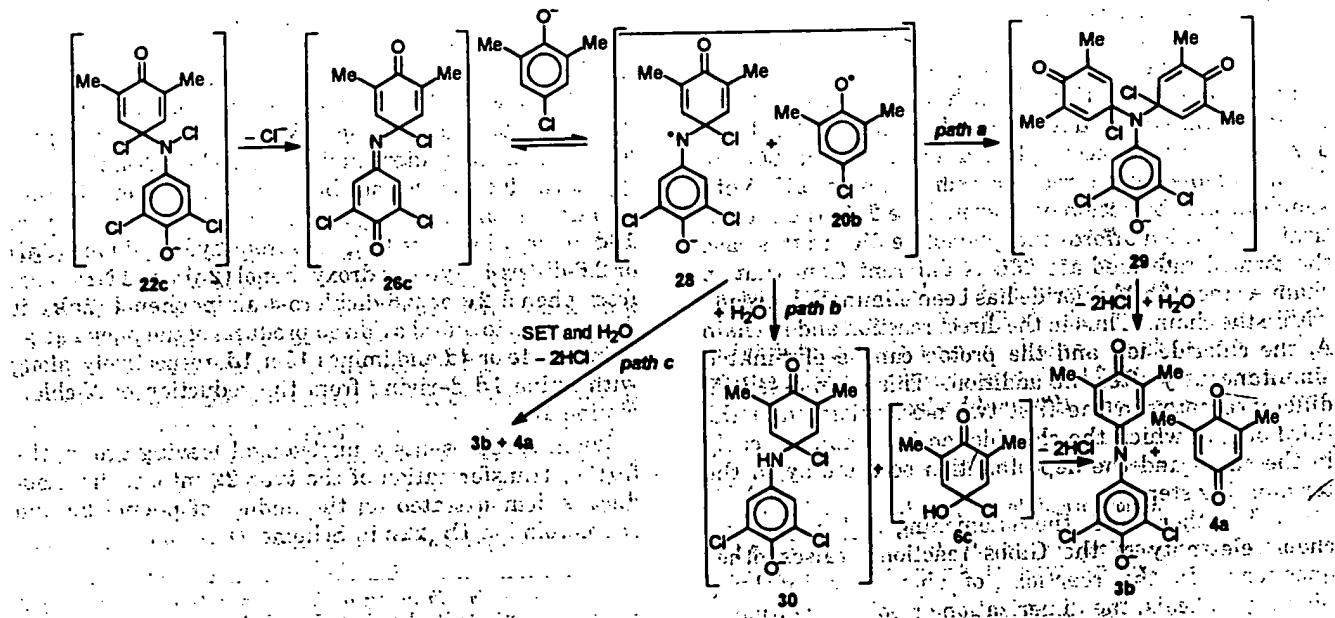
Scheme 5



Scheme 6



Scheme 7



It is evident that Cl cannot be eliminated as an anion from intermediate 26c, the chloride-eliminated product of 22c. Therefore, it oxidizes a second molecule of phenol 2c, which is in full agreement with the established

stoichiometry. The oxidation of the second phenol molecule was investigated as well. If this oxidation is presumed to be a SET with a chain reaction, the formed phenoxyl radical can be trapped by oxygen to give hydro-

Table 6. Reactions of Intermediates 10a-c with Phenols<sup>a</sup>

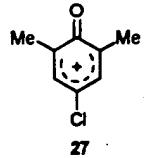
entry	intermediate	parent phenol, $E_{1/2}$ , (V) <sup>b</sup>	second phenol, $E_{1/2}$ , (V) <sup>b</sup>	intramolecular indophenol, %, intermolecular, %
1		2i 0.12	2c 0.19	67 3b 33
2	10a		2h 0.23	100 3f 0
3			2ac 0.42	100 3f 0
4		2g -0.01	2c 0.19	29 3b 71
5	10b		2h 0.23	75 3f 25
6			2ah 0.11	99 3b <sup>c</sup> 1
7		2j 0.15	2c 0.19	75 3b 25
8			2f 0.03	100 3e 0
9	10c		2u -0.35	100 3e 0
10			2t 0.05	no reaction

<sup>a</sup>For details see experimental section.<sup>b</sup> $E_{1/2}$  was determined in borate buffer (pH = 9.2) at 298 K.<sup>c</sup>In water the rate was the same.

peroxide, which is known to transform into quinol in an alkaline medium.<sup>51</sup> To check this hypothesis hydroperoxide **6b** was synthesized and its stability was examined. However, under the conditions of the Gibbs reaction, it remained unchanged and could not be converted into quinol **6a**. On the other hand, **6a** was formed even in those cases when the reaction was performed under argon. Accordingly, **6a** can be considered as the primary oxidation product of phenol **2g**. The formation of indophenols from *N*-chloroimine **1e** and phenols **2g**, **2f**, or **2ah** could be prevented by scavenger DCNB, but it cannot when intermediate **10b** and a second phenol molecule are applied; these facts suggest a mechanism, in which the first oxidation step, the formation of the intermediate **22**, is a SET with chain reaction, like the reactions of **2a** with **1e** and, in the presence of an additive, with **1b**, whereas the second oxidation step, the formation of the indophenol and the oxidized phenol, is not. This second oxidation step was further investigated by reducing intermediates **10a-c** with phenols being different from that forming the intermediate. In this way, information can be obtained on the role of the second phenol molecule whether it just reduces the intermediate affording intramolecular indophenol or whether it substitutes the nitrogen, which would result in an exchange of the parent and the attacking phenols to afford intermolecular indophenol or the mixture of these two. Determination of the rate of these intra- and intermolecular indophenols can allow these questions to be answered. In these experiments our aim was to compare the redox potentials and the steric effects of the phenols that form the intermediates with the characteristics of the phenols reducing them, in water or in TCE, respectively. In water only intramolecular indophenols were formed. However, in TCE, in several cases both indophenols were formed indicating some exchange reaction. In Table 6, the polarographic half-wave oxidative potentials ( $E_{1/2}$ ) of the parent as well as the reducing phenols and the percentage of the intra- and intermolecular indophenols are summarized. Applying phenol **2c** to reduce intermediates **10a-c**, the lower was the  $E_{1/2}$  of the parent

phenol, i.e., the more oxidizable it was, the more intermolecular indophenol was formed (entries 1, 4, and 7). The same is true for **2h** (entries 2 and 5).

In the last two entries, two reducing phenols (**2u** and **2t**) carrying an electrofugal leaving group at C-4 are also depicted. These experiments indicate that the electron transfer proceeds from the *para* position of the reducing phenol; when it is hindered there is no oxidation at all. Previous experiments demonstrated that this step is not a chain reaction. It was attractive to suppose a SET for this redox step also, although the formation of the quinone derivatives implied that a way *via* phenoxenium ion<sup>52</sup> **27** also should be considered. Comparing the heats



of formation of the possible intermediates (Table 8), we found that the redox reaction of intermediate **26c** and phenol **2c** probably cannot afford the free phenoxenium ion<sup>53</sup> **27**, but rather a SET from phenol **2c** to **26c** can proceed (Scheme 7). For the further transformation of the radical pair, involving amine radical **28** and phenoxy radical **20b** in the solvent cage, three pathways are proposed: combination of these radicals (path a) affords tertiary amine **29**, which will hydrolyze to quinone **4a** and indophenol **3b**. These products are formed also either *via* hydrogen and hydroxyl abstraction from water by the radical pair (path b), or *via* another SET from phenoxy radical **20b** to amine radical **28** and a concerted water addition (path c) yielding indophenol **3b** and

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(53) A significantly exothermic solvation of this cation can make the process possible.

**Table 7. Squares of LCAO Coefficients of the HOMOs for *Para*-Substituted Phenolate Ion and the SHOMOs for Phenoxy Radical Derivatives**

atom	anions			radicals		
	R:H	R:F	R:Me	R:H	R:F	R:Me
C <sub>i</sub>	0.03	0.03	0.03	0.02	0.02	0.02
C <sub>o</sub>	0.23	0.22	0.22	0.22	0.20	0.20
C <sub>m</sub>	—	—	—	0.28 <sup>a</sup>	—	0.25 <sup>a</sup>
C <sub>p</sub>	0.00	0.00	0.00	0.00	0.01	0.01
C <sub>p</sub>	0.30	0.30	0.30	0.38	0.40	0.39
C <sub>p</sub>	—	—	—	0.42 <sup>a</sup>	—	0.44 <sup>a</sup>

<sup>a</sup> Calculated spin densities based on ESR experiments; see ref 50.

**Table 8. Computed PM3<sup>60</sup> Energies of Selected Reactants, Potential Reaction Intermediates, and Products of the Gibbs Reaction**

comp label	energy, kcal mol <sup>-1</sup>	comp label	energy, kcal mol <sup>-1</sup>
1b	+3.3	24a	+56.2
2a	-44.1	24a <sup>-</sup>	-3.3
2c	-74.2	25a	-55.9
3b	-82.1		(-53.4) <sup>a</sup>
3f	-65.1	26a	+8.9
4a	-49.6	26c	-13.4
6c	-71.2	27	+170.6
20a	+3.3	28	-81.4
20b	-23.2	29	-108.6
21a	-60.8	30	-95.1
22a	-79.2 (-71.5) <sup>a</sup>	Cl <sup>-</sup>	-51.5
		HCl	-20.5
23a	-7.5 (-7.2) <sup>a</sup>	H <sub>2</sub> O	-53.4

<sup>a</sup> Energy of the *ortho* isomer.

quinone 4a via quinamine 30 and quinole 6c (see ref 52e). It is evident that the decomposition of the tertiary amine 29, to a given mixture of indophenols will depend on the oxidizability of the phenols involved, i.e.,  $E_{1/2}$  (see entries 1, 4, and 7 or 2 and 7 in Table 6).

### Quantum Chemical Calculations

**Methods.** A modified hybrid version of MOPAC 5.00 program,<sup>54</sup> labeled as MOPAC 5.50, has been used throughout the computations. The modification included the incorporation of the EF<sup>55</sup> and the GDIIS<sup>56</sup> optimization methods, from MOPAC 6.00 program<sup>57</sup> and TX90 program,<sup>58</sup> respectively. More important was the fact that the routines of Pulay's TX90,<sup>59</sup> necessary for the automatic generation<sup>58</sup> and use of *natural internal coordinates* were also incorporated. The modified hybrid MOPAC 5.50 was found to be reliable and fast during geometry optimization in the natural internal coordinates with the efficient use of the updated Hessian matrix in each successive cycle.<sup>58</sup> Since some of the molecules had open electron shells, all molecules (even those that had closed electron shells) were studied within the UHF formalism. Full conformational study was carried out wherever the molecular flexibility allowed the formation of different conformers. However, only the global minima are reported in this paper.

(54) Frank, J. MOPAC 5.00 QCPE No. 455, Seiler Res. Lab., U.S. Air Force Academy, Colorado Springs, CO 80840.  
 (55) Baker, J. J. Comput. Chem. 1986, 7, 385-395.  
 (56) Csaszar, P.; Pulay, P. J. Mol. Struct. 1984, 114, 31.  
 (57) Frank, J. MOPAC 6.00 QCPE No. 455, Seiler Res. Lab., U.S. Air Force Academy, Colorado Springs, CO 80840.  
 (58) Fogarasi, G.; Zhou, X.; Taylor, P. W.; Pulay, P. J. Am. Chem. Soc. 1992, 114, 8191-8201.  
 (59) (a) Pulay, P. TX90, 1990, Fayetteville, AK. (b) Pulay, P. Theor. Chim. Acta 1979, 50, 229.

**Sc pe.** The strong *para* selectivity is a predominant feature of the Gibbs reaction; therefore, the primary question, whether the aromatic substitution took place on the anion of 2a or on the phenoxy radical (20a), had to be dealt with. This made the analysis of the electronic structures of the reactants necessary. In particular, the electron or spin density of the HOMO of the reacting ion or single highest occupied molecular orbital (SHOMO) of radical 20a, respectively, was of particular importance. Since the primary reactant is the phenolate ion, for the free radical mechanism the radical 20a had to be formed by SET which opened up the realms of possibilities for chain reaction mechanisms.

The main purpose of the computation was to compare the energetics of the intermediates of potential reaction mechanisms. The energetics of the reactions are presented as relative values with respect to the reactant state.

**Results.** The squares of the LCAO coefficients of the HOMO for the phenolate and radical 20a are summarized in Table 7 for a number of substituents. This table clearly indicates that the squares of the LCAO coefficients of HOMO are changing proportionally with the *para* substituent. Consequently, a given substituent (e.g., F) in the *para* position will not redirect the Gibbs reaction to the *ortho* position but rather it departs during the substitution and the *para* isomer is formed. From the data presented in Table 7 it is clear that the partial electron density difference in the *para* position is greater in the case of the radical 20a than in the case of the phenolate ion favoring the *para* position. Consequently, if the reaction is occurring from the radical 20a formed via SET the *para* selectivity of the subsequent reaction is practically guaranteed. The question whether the reaction is indeed occurring from the radical 20a can only be answered from the knowledge of the energetics associated with the potential reaction mechanism. If we take the SHOMO electron density of the radical 20a to be equal to the spin density then the squares of the LCAO coefficients of SHOMO may be compared to the calculated spin densities<sup>50</sup> based on ESR experiments. The comparison is favorable (Table 7). The computed total energies of selected compounds can be found in Table 8. The energetics for a selected pair of reactants, their possible reaction intermediates associated with potential reaction mechanisms, and final products are summarized in Table 9. These energies were combined for the SET process as well for the three potential reaction mechanisms: I, direct; II, chain A; III, chain B. The energetics are presented graphically in Figure 5. These results clearly support the previous conclusion that mechanism I and II are similar and III is completely different. However this energy level diagram also suggests that mechanisms I and II are favored, at least in the thermodynamic sense, over mechanism III. Although it may be conceivable that solvation might modify the computed energy differences, nevertheless, the qualitative nature of the conclusion, in general, is predicted to be valid.

### Summary and Conclusions

The stoichiometry of the Gibbs reaction, indophenol 3 formation from phenol 2 with *N*-chlorobenzoquinone imines 1, is 1:1 when the *para* substituent (R) of the phenol is an electrofugal leaving group, while it is 2:1 when R is a nucleofugal leaving group. The first step of the reaction, which is rate-determining in several cases,

Table 9. Computed and Relative Energetics (kcal mol<sup>-1</sup>) of Potential Reaction Mechanisms

Initial state			Final state	
	a.	2a,1b → 20a,21a		
		-40.8	-57.6	
		0.0	-16.8	
b.	2a,1b → 20a,21a		22a → 3f (HCl)	
		-40.8	-72.9	-85.6
		0.0	-32.2	-44.8
c.	20a,1b → 23a,2a (2a)	23a,2a → 22a (20a)	22a → 3f (20a,HCl)	
		-37.5	-51.6	-69.7
		0.0	-14.1	-32.2
				-82.4
d.	21a → 24a,2a (2a,1b)	25a,1b → 26a (21a,CT)	26a → 3f (21a,HCl)	
		-101.6	-104.1	-103.5
		0.0	+65.5	-1.9
				-146.4
				-44.8

a. SET reaction.

b. Direct reaction

c. Chain A

d. Chain B

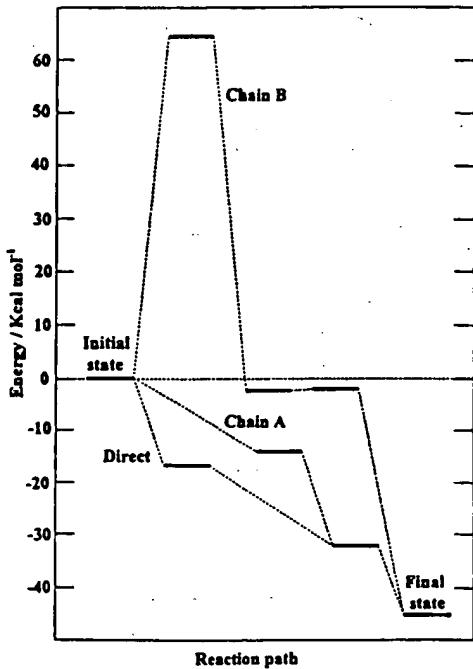


Figure 5. PM3 energy level diagrams for potential reaction mechanisms. For more details see Table 9.

is a SET from phenolate to *N*-chloroimine 1. When R is a nucleofugal leaving group, the reaction goes through an intermediate. In these cases the slow step is another SET from phenolate to this intermediate; several of them could be isolated due to the large difference between the rates of these SETs. In these cases, if we want to obtain the indophenol 3, it is practical to convert *N*-chloroimine 1 (with alcohol or 2,6-dichloro-4-aminophenol) to benzoquinone imine.<sup>1a</sup> For these radical reactions two different alternatives are suggested: either a combination of the radicals, formed by a SET, in the solvent cage or, if they can escape from this, a chain reaction. The particular pathway depends on the reactivity of the radical and the character of the solvent. When these pathways ran parallel, in some cases, they could be separated or

transformed one to the other. The reaction shows an extremely high *para* selectivity even if the substitution does follow radical mechanism. Spin density data calculated by semiempirical quantum chemical methods and from ESR measurement<sup>50</sup> are in good agreement with the observed *para* selectivity.

## Experimental Section

Reaction kinetics were measured UV spectrophotometrically by assaying the concentration of indophenols 3 in an aqueous solution containing 1% (7% in the assay of 2d, 2e, and 2ai) acetonitrile, at 25 °C, and the pH was adjusted to 9.2 by borate buffer. If required, the pH was decreased by adding hydrochloric acid (0.1 M), besides maintaining the ionic strength with NaCl solution. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded by a Bruker AC 250 spectrometer equipped with an ASPECT 3000 computer, at frequencies of 250.1 and 62.9 MHz, respectively. Unless otherwise noted, all NMR spectra were recorded in acid free 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> (TCE) with tetramethylsilane (TMS) and TCE (73.8 ppm) as reference standards. In the experiments, <sup>1</sup>H, <sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H NOE, <sup>13</sup>C, DEPT, selective INEPT,<sup>61</sup> proton-coupled <sup>13</sup>C (gated), selective proton-decoupled <sup>13</sup>C, <sup>13</sup>C-<sup>1</sup>H COSY, measurements were applied.<sup>62</sup> In many cases unstable structures, detectable only in solution, were elucidated. These compounds were assigned as part of multicomponent systems in which the signals of the known compounds were confirmed by adding them prepared in a different route into the solution recorded. ESR measurements were carried out on JES-ME-3X spectrometer at ambient temperature. Polarographic measurements were carried out with a PAR 174-A Polarographic Analyser (glassy carbon PT and SCE electrodes) in the aqueous,  $1.224 \times 10^{-4}$  mol dm<sup>-3</sup> solution of the test compound buffered by Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, at dc operation. 4-Deuteriophenol was prepared from Grignard compound by D<sub>2</sub>O. 1b was purchased from Merck, further benzoquinone *N*-chloroimines were prepared by the known method,<sup>63</sup> and preparation of 1g was carried out in a two-phase system of hexane-water with a fast extraction of 1g into hexane. Computations were carried out on an IBM RISC 6000/320 and 560 workstation in the

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Department of Theoretical Chemistry of the L. Eötvös University Budapest.

**Reaction of 2,6-Di-*tert*-butyl-4-chlorophenol (2f) with 1b.** To a solution of 1b (31 mg, 0.15 mmol) in *tert*-butyl alcohol (10 mL) was poured a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and then a solution of 2f (90 mg, 0.37 mmol) in *tert*-butyl alcohol (30 mL) was added. The mixture was kept at ambient temperature (25 °C) for 20–25 min and then the solution was shaken with hexane (100 mL), the pH was adjusted to 6.5–7.0 (6.5 mL, 0.5 M HCl), and after repeated shaking, the two layers were separated. The extraction was repeated with 100 mL of solvent. The organic extracts were combined, washed with water (2 × 100 mL), dried over anhydrous sodium sulfate, and concentrated to 4–5 mL at reduced pressure (water bath temperature 30–35 °C). After addition of TCE (0.5 mL) the rest of the hexane was removed. The molar ratio of the products 3e:4d:5 was 1:1:2 by <sup>1</sup>H NMR. (Spectroscopic data of 5 are listed in part 2 of this series). 4d: <sup>1</sup>H NMR δ 6.49 (s, 2H), 1.26 (s, 18H); <sup>13</sup>C NMR δ 188.4 (s), 187.5 (s), 157.7 (s), 129.9 (d), 35.4 (s), 29.3 (q). The stability of 5 (see part 2) was markedly affected by the acidity of the solvent, but in water and acid-free TCE the rate of conversion to indophenol 3e could be significantly suppressed (no significant transformation was detected at 250 K during 3 days). <sup>1</sup>H NMR spectra of the indophenol 3e is sensitive to both acid and alteration of temperature. Since the transformation of compound 5 to 4d and indophenol 3e is an acid-producing step, the δ<sub>H</sub> values of 3e depend on time. <sup>1</sup>H NMR spectra of 3e were recorded within 20 min at 298 K: δ 7.25 (s, br, 1H), 7.05 (s, br, 2H), 6.85 (d, J = 2.5 Hz, 1H). After compound 5 was converted to indophenol 3e, dichloromethane (30 mL) was added to the solution, it was washed first with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (0.05 M, 2 × 10 mL) and subsequently with water (10 mL) and dried, and the dichloromethane was removed by evaporation under reduced pressure. 2,6-Bis(1,1-dimethylethyl)-4-[(3,5-dichloro-4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (3e): <sup>1</sup>H NMR δ 6.97 (d, J = 2.5 Hz, 1H), 6.89 (s, 2H), 6.77 (d, J = 2.5 Hz, 1H), 1.31 (s, 9H), 1.22 (s, 9H); <sup>13</sup>C NMR δ 187.3 (s), 159.5 (s), 154.4 (s), 153.4 (s), 145.5 (s), 142.6 (s), 134.1 (d), 121.5 (s), 121.3 (d), 120.8 (d), 35.7 (s), 35.2 (s), 29.3 (q).

**Reaction of 2,6-Dimethyl-4-chlorophenol (2c) with 1b.** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (21 mg, 0.1 mmol) in acetonitrile (10 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2c (40 mg, 0.25 mmol) in acetonitrile (10 mL) with 20 min reaction time. The molar ratio of the products 3b:4a was 1:1 by <sup>1</sup>H NMR. 2,6-Dimethyl-4-[(3,5-dichloro-4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (3b): <sup>1</sup>H NMR δ 7.03 and 6.81 (sextet, J = 2.7, 1.4 Hz, 2H), 6.86 (s, 2H), 2.08 (d, J = 1.4 Hz, 3H), 2.01 (d, J = 1.4 Hz, 3H). 4a: <sup>1</sup>H NMR δ 6.55 (q, J = 0.5 Hz, 2H), 2.04 (d, J = 0.5 Hz, 6H); <sup>13</sup>C NMR δ 188.1 (s), 187.7 (s), 145.7 (s), 133.1 (d), 15.9 (q).

**Reaction of 2,6-Di-*tert*-butyl-4-methoxyphenol (2g) with 1b. Method a:** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (17 mg, 0.08 mmol) in acetonitrile (10 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2g (47 mg, 0.2 mmol) in acetonitrile (20 mL) with 10 min reaction time. The molar ratio of the products 3e:6:4d was 2:1:1 by <sup>1</sup>H NMR. The <sup>1</sup>H and <sup>13</sup>C NMR data of 3e and 4d are listed at the reactions of 2f and 1b. The NMR spectra should be immediately recorded after processing since quinol 6a rapidly transforms into quinone 4d. 2,6-Bis(1,1-dimethylethyl)-4-hydroxy-4-methoxy-2,5-cyclohexadien-1-one (6): <sup>1</sup>H NMR δ 6.56 (s, 2H), 6.0–6.4 (OH, 1H), 3.40 (s, 3H), 1.21 (s, 18H); <sup>13</sup>C NMR δ 186.4 (s), 149.4 (s), 131.4 (d), 97.3 (s), 50.7 (q), 35.0 (s), 29.3 (q). **Method b:** The same procedure as described for method a was applied using a solution of 1b (21 mg, 0.1 mmol) in acetonitrile (10 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2g (24 mg, 0.1 mmol) in acetonitrile (20 mL). After 3–4 min the reaction mixture was processed as described above without giving TCE, with evaporation to dryness (water bath temperature 25 °C) at reduced pressure. The molar ratio of the products 10b:1b:3e:6:4d was 20:6:3:1:2 by <sup>1</sup>H NMR. At ambient temperature compound

10b decomposes within minutes; thus, the dry residue obtained after evaporation should be immediately dissolved in cold, acid-free CDCl<sub>3</sub>, and the NMR spectra should be recorded immediately.

2,6-Bis(1,1-dimethylethyl)-4-methoxy-4-[(3,5-dichloro-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10b): <sup>1</sup>H NMR (CDCl<sub>3</sub>, T = 264 K) δ 7.69 (d, J = 2.5 Hz, 1H), 7.36 (d, J = 2.5 Hz, 1H), 6.39 (s, 2H), 3.29 (s, 3H), 1.27 (s, 18H); <sup>13</sup>C NMR (T = 263 K) δ 185.1 (s), 172.9 (s), 154.4 (s), 149.3 (s), 140.1 (d), 139.2 (s), 137.0 (s), 136.0 (d), 125.7 (d), 88.0 (s), 50.8 (q), 35.2 (s), 29.2 (q). After recording the NMR spectra, either phenol 2ah, 2i, or 2c was added. After 15 min, in the first two cases, only indophenol 3e was obtained, but the reaction of 2c and 10b gave a mixture of indophenols 3e and 3b (1:2.5). The reaction of 10b with 2ah and 2c was carried out in water, too: the dry residue, obtained on evaporation of the hexane solution, was dissolved in tetrahydrofuran (60 mL), water (400 mL) and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (0.05 M, 50 mL) were added, this solution was halved, and either 2ah or 2c (10 mg) in THF (2 mL) was added. After 15 or 50 min, the reaction mixture was processed the known way to record the <sup>1</sup>H NMR spectra. In both cases only indophenol 3e was formed, and 3b could not be detected.

**Reaction of 2-*tert*-Butyl-4-methoxyphenol (2i) with 1b.**

**Method a:** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (42 mg, 0.2 mmol) in acetonitrile (10 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2i (144 mg, 0.8 mmol) in acetonitrile (20 mL) with 10 min reaction time. The molar ratio of the products 3g:7b:8a was 4:3:1 by <sup>1</sup>H NMR. Subsequently, the TCE solution was diluted with dichloromethane (50 mL), washed with NaOH (0.1 M, 2 × 70 mL) and water (2 × 60 mL), dried, and evaporated at reduced pressure to dryness. 7b and 8a were separated by column chromatography (1:1 benzene/hexane). 3g was isolated from the alkaline solution after neutralization and subsequent extraction with dichloromethane. 7b: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.96 (d, J = 3.0 Hz, 2H), 6.62 (d, J = 3.0 Hz, 2H), 5.02 (s, OH, 2H), 3.77 (s, 6H), 1.43 (s, 18H); <sup>13</sup>C NMR δ 153.2 (s), 145.9 (s), 138.9 (s), 123.2 (s), 115.3 (d), 111.8 (d), 55.8 (q), 35.2 (s), 29.5 (q). 8a: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.96 (d, J = 2.9 Hz, 1H), 6.75 (d, J = 8.8 Hz, 1H), 6.66 (dd, J = 8.8, 2.9 Hz, 1H), 6.59 (d, J = 2.9 Hz, 1H), 6.18 (d, J = 2.9 Hz, 1H), 5.60 (s, OH), 3.80 (s, 3H), 3.64 (s, 3H), 1.44 (s, 9H), 1.42 (s, 9H); <sup>13</sup>C NMR δ 155.5 (s), 152.1 (s), 148.9 (s), 145.2 (s), 142.2 (s), 140.1 (s), 137.3 (s), 120.6 (d), 113.9 (d), 110.9 (d), 107.2 (d), 101.0 (d), 55.7 (q), 55.6 (q), 35.0 (s), 34.9 (s), 30.3 (q), 29.4 (q). 3g: <sup>1</sup>H NMR (CDCl<sub>3</sub>, mixture of Z and E isomers) δ 7.08 (6.92) (d, J = 2.8 Hz, 1H), 6.98 (7.12) (dd, J = 9.9, 2.8 Hz, 1H), 6.87 (6.90) (s, 2H), 6.49 (6.58) (d, J = 9.9 Hz, 1H), 1.32 (1.23) (s, 9H). If the molar ratio of 2i and 1b was not 4:1 but 2.5:1 in the reaction mixture, 9 was also formed besides 7b and 8a (7b:8a:9 ≈ 5:1:2). 9: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.99 (d, J = 3.0 Hz, 1H), 6.72 (d, J = 2.5 Hz, 1H), 6.67 (d, J = 2.5 Hz, 1H), 6.50 (d, J = 3.0 Hz, 1H), 6.26 (s, OH), 3.77 (s, 3H), 1.44 (s, 9H), 1.34 (s, 9H); <sup>13</sup>C NMR δ 189.7 (s), 187.9 (s), 157.0 (s), 153.5 (s), 149.3 (s), 146.1 (s), 141.1 (s), 135.0 (d), 131.7 (d), 124.8 (s), 116.7 (d), 112.3 (d), 55.7 (q), 35.7 (s), 35.2 (s), 29.8 (q), 29.3 (q). **Method b:** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (42 mg, 0.2 mmol) in acetonitrile (10 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2i (36 mg, 0.2 mmol) in acetonitrile (20 mL) with 2–3 min reaction time. The hexane layer was washed with Na<sub>2</sub>CO<sub>3</sub> solution (0.1 M, 2 × 100 mL) and water (2 × 50 mL). After drying, the organic layer was concentrated to 4–5 mL at reduced pressure, TCE was added, and the residual hexane was removed by evaporation. 3g was isolated from the carbonate solution after neutralization and subsequent extraction with dichloromethane. (Assignment: see under method a). Without washing the solution with Na<sub>2</sub>CO<sub>3</sub>, the molar ratio of the products 1b:3g:10a was 2:5:4 by <sup>1</sup>H NMR, in TCE. 2-(1,1-Dimethylethyl)-4-methoxy-4-[(3,5-dichloro-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10a): <sup>1</sup>H NMR δ 7.82 (d, J = 2.5 Hz, 1H), 7.38 (d, J = 2.5 Hz, 1H), 6.63 (dd, J = 9.9, 3.0 Hz, 1H), 6.42 (d, J = 3.0 Hz, 1H), 6.35 (d, J = 9.9 Hz, 1H), 3.32 (s, 3H), 1.26 (s, 9H); <sup>13</sup>C NMR (T = 268 K) δ 184.7 (s),

173.0 (s), 154.8 (s), 148.0 (s), 142.3 (d), 140.4 (d), 139.2 (s), 138.7 (d), 136.8 (s), 131.8 (d), 126.2 (d), 88.1 (s), 51.2 (q), 34.8 (s), 28.8 (q). An experiment was also performed without working up the aqueous solution after standing for 2–3 min, but 2i (40 mg, 0.22 mmol) in acetonitrile (20 mL) was added instead. Then the reaction mixture was processed in the usual way after 10 min. The recorded <sup>1</sup>H NMR spectra indicated the presence of 3g, 7b, and 8a, suggesting that the redox reaction of 10a and 2i also yielded 7b and 8a in addition to 3g. (When 2i was added to the solution containing compound 10a, and monitored by <sup>1</sup>H NMR, only 10a reacted with the phenol derivative added, while 1b did not. In TCE solution, compounds 3g, 7b, and 8a formed).

**Reaction of 4-Methoxyphenol (2h) with 1b.** To a solution of 1b (21 mg, 0.1 mmol) in acetonitrile (10 mL) were added a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M) and then a solution of 2h (25 mg, 0.2 mmol) in acetonitrile (10 mL). After 20 min the reaction mixture was extracted with hexane (100 mL) and, after neutralization with HCl (3.3 mL, 1 M), with dichloromethane (2 × 80 mL). The dichloromethane layer was dried and evaporated. 3f and 7a were separated from this residue by prep TLC (silica, diisopropyl ether). 7a: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.96 (d, *J* = 8.8 Hz, 2H), 6.86 (dd, *J* = 8.8, 2.9 Hz, 2H), 6.81 (d, *J* = 2.9 Hz, 2H) 5.7–5.2 (OH, 2H), 3.80 (s, 6H); <sup>13</sup>C NMR δ 154.2 (s), 146.6 (s), 124.9 (s), 117.7 (d), 115.9 (d), 115.5 (d), 55.8 (q).

**Reaction of Hydroquinone 4-Methoxybenzyl Ether (2j) with 1b.** To a solution of 1b (53 mg, 0.25 mmol) in *tert*-butyl alcohol (15 mL) were added a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M) and then a solution of 2j (58 mg, 0.25 mmol) in *tert*-butyl alcohol (15 mL). After 50 min the reaction mixture was extracted with dichloromethane as described for the preparation of 5 then the organic layer was washed with Na<sub>2</sub>CO<sub>3</sub> (0.1 M, 100 mL) and water (2 × 60 mL), dried, and then processed as described for 5. 3f was isolated from the carbonate solution by neutralization and extraction with dichloromethane. In this case, 4-methoxybenzyl alcohol (31) deriving from the *para* leaving group could be detected. Before washing the solution with Na<sub>2</sub>CO<sub>3</sub>, the molar ratio of the products 3f:31:10c:1b was 1:1.1:0.5:0.5 by <sup>1</sup>H NMR, in TCE. 31: <sup>1</sup>H NMR δ 7.27 (d, *J* = 9.5 Hz, 2H), 6.90 (d, *J* = 9.50 Hz, 2H), 4.58 (s, 2H), 3.78 (s, 3H); <sup>13</sup>C NMR δ 158.7 (s), 132.8 (s), 128.8 (d), 113.7 (d), 64.7 (t), 55.3 (q). 3f: <sup>1</sup>H NMR (2:1 mixture of tautomers 3fa and 3fb) 4-[{(3,5-dichloro-4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (3fa): δ 7.27 (dd, *J* = 10.0, 2.6 Hz, 1H), 7.11 (dd, *J* = 10.3, 2.6 Hz, 1H), 6.92 (s, 2H), 6.70 (dd, *J* = 10.0, 2.6 Hz, 1H), 6.60 (dd, *J* = 10.3, 2.6 Hz, 1H); 2,6-dichloro-4-[{(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (3fb): δ 7.57 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 6.95 (s, 4H); 4-[{(4-methoxybenzyl)oxy]-4-[{(3,5-dichloro-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10c): <sup>1</sup>H NMR δ 8.00 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.23 (d, *J* = 9.5 Hz, 2H), 6.87 (d, *J* = 9.5 Hz, 2H), 6.79 (d, *J* = 10.0 Hz, 2H), 6.42 (d, *J* = 10.0 Hz, 2H), 4.50 (s, 2H), 3.79 (s, 3H); <sup>13</sup>C NMR (*T* = 265 K) δ 184.6 (s), 173.1 (s), 159.2 (s), 155.7 (s), 145.2 (d), 140.4 (s), 139.4 (d), 137.0 (d), 129.8 (d), 129.7 (d), 128.6 (s), 126.6 (s), 113.8 (d), 87.0 (s), 66.3 (t), 55.4 (q). If phenol 2j was added to the solution containing compound 10c, according to <sup>1</sup>H NMR, in addition to 3f and 31, several unidentified compounds giving methylene signals were formed, resulting probably from the reactions of the oxidized phenols formed in the TCE solution. (Only 10c reacts with the phenol derivative added to the solution under these circumstances; 1b does not). The finding that 3f and 31 were formed in a molar ratio of 1:1, similarly to the reaction carried out in aqueous solution, suggested that the oxidized phenol failed to yield 31.

**Reaction of 4-Methylphenol (2l) with 1b.** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (126 mg, 0.6 mmol) in acetonitrile (20 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2l (22 mg, 0.2 mmol) in acetonitrile (5 mL) with 5 min reaction time. 2,6-Dichloro-4-[{(1-methyl-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10d): <sup>1</sup>H NMR δ 7.34 (d, *J* = 2.5 Hz, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.05 (d, *J* = 10.0 Hz, 2H), 6.37 (d, *J* = 10.0 Hz, 2H),

1.80 (s, 3H); <sup>13</sup>C NMR δ 184.4 (s), 172.8 (s), 157.8 (s), 152.3 (d), 140.4 (d), 139.8 (s), 136.7 (s), 127.1 (d), 123.7 (d), 62.8 (s), 31.5 (q). 1b: <sup>1</sup>H NMR δ 7.99 (d, *J* = 2.5 Hz, 1H), 7.51 (d, *J* = 2.5 Hz, 1H); <sup>13</sup>C NMR δ 172.8 (s), 165.1 (s), 141.5 (s), 136.8 (s), 134.5 (d), 124.4 (d). Signals of 1b were verified by adding more 1b to the solution recorded.

**Reaction of 2,4-Dimethylphenol (2m) with 1b.** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (126 mg, 0.6 mmol) in acetonitrile (20 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2m (24 mg, 0.2 mmol) in acetonitrile (5 mL) with 5 min reaction time. 2,6-Dichloro-4-[{(1,3-dimethyl-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10e): <sup>1</sup>H NMR δ 7.34 (d, *J* = 2.5 Hz, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.02 (dd, *J* = 9.9, 3.3 Hz, 1H), 6.80 (sextet, *J* = 3.3, 1.5 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 1.95 (d, *J* = 1.5 Hz, 3H), 1.78 (s, 3H); <sup>13</sup>C NMR δ 185.0 (s), 172.8 (s), 157.4 (s), 152.1 (d), 147.6 (d), 140.5 (d), 139.5 (s), 136.5 (s), 133.8 (s), 126.8 (d), 123.9 (d), 63.1 (s), 31.6 (q), 15.7 (q).

**Reaction of 2,6-Di-*tert*-butyl-4-methylphenol (2n) with 1b.** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (63 mg, 0.3 mmol) in acetonitrile (10 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2n (24 mg, 0.1 mmol) in acetonitrile (5 mL) with 5 min reaction time. 2,6-Dichloro-4-[{(3,5-bis-(1,1-dimethylethyl)-1-methyl-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10f): <sup>1</sup>H NMR δ 7.32 (d, *J* = 2.5 Hz, 1H), 7.26 (d, *J* = 2.5 Hz, 1H), 6.64 (s, 2H), 1.72 (s, 3H), 1.23 (s, 18H); <sup>13</sup>C NMR δ 185.3 (s), 172.9 (s), 157.4 (s), 144.6 (d), 143.6 (d), 140.4 (d), 138.6 (s), 136.4 (s), 124.3 (d), 62.4 (s), 34.6 (s), 31.7 (q), 29.0 (q).

**Reaction of 3,4-Dimethylphenol (2o) with 1b.** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (126 mg, 0.6 mmol) in acetonitrile (20 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2o (24 mg, 0.2 mmol) in acetonitrile (5 mL) with 5 min reaction time. 2,6-Dichloro-4-[{(1,2-dimethyl-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10g): <sup>1</sup>H NMR δ 7.37 (d, *J* = 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.99 (d, *J* = 10.0 Hz, 1H), 6.32 (dd, *J* = 10.0, 1.7 Hz, 1H), 6.21 (quintet, *J* = 1.7, 1.4 Hz, 1H), 1.92 (d, *J* = 1.4 Hz, 3H), 1.83 (s, 3H); <sup>13</sup>C NMR δ 184.8 (s), 172.7 (s), 163.4 (s), 158.0 (s), 152.6 (d), 140.2 (s), 140.1 (d), 136.6 (s), 126.7 (d), 126.2 (d), 123.0 (d), 65.1 (s), 31.2 (q), 19.2 (q).

**Reaction of 2,4,6-Trimethylphenol (2p) with 1b.** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (126 mg, 0.6 mmol) in acetonitrile (20 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M), and a solution of 2p (26 mg, 0.2 mmol) in acetonitrile (5 mL) with 5 min reaction time. 2,6-Dichloro-4-[{(1,3,5-trimethyl-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10h): <sup>1</sup>H NMR δ 7.27 (d, *J* = 2.5 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 6.75 (s, 2H), 1.89 (s, 6H), 1.70 (s, 3H); <sup>13</sup>C NMR δ 185.6 (s), 172.8 (s), 156.9 (s), 147.4 (d), 140.5 (d), 139.1 (s), 136.2 (s), 133.2 (s), 124.0 (d), 62.8 (s), 31.6 (q), 15.8 (q).

**Reaction of 2,4,6-Tri-*tert*-butylphenol (2q) with 1b.** The same procedure, but under argon atmosphere as described for the reaction of 2f and 1b was applied using solutions being kept under argon gas flow for 30 min before the reaction, of 1b (106 mg, 0.5 mmol) in acetonitrile (15 mL), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6 × 10<sup>-3</sup> M) and 2q (39 mg, 0.15 mmol) in acetonitrile (25 mL) with 25 min reaction time (1b:10i:12b ≈ 1:0.22:0.18 by <sup>1</sup>H NMR). 2,6-Dichloro-4-[{(1,3,5-tris(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (10i): <sup>1</sup>H NMR (*T* = 278 K) δ 7.40 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 2.5 Hz, 1H), 6.53 (s, 2H), 1.21 (s, 18H), 1.00 (s, 9H); <sup>13</sup>C NMR (*T* = 278 K) δ 185.7 (s), 173.2 (s), 157.8 (s), 146.6 (s), 141.8 (d), 140.9 (d), 138.2 (s), 136.0 (s, overlapping a signal of 1b), 124.7 (d), 70.0 (s), 42.5 (s), 35.0 (s), 29.1 (q), 25.6 (q). 2,6-Dichloro-4-[{(1,3,5-tris(1,1-dimethylethyl)-6-oxo-2,5-cyclohexadienyl)imino]-2,5-cyclohexadien-1-one (12b): <sup>1</sup>H NMR (*T* = 278 K) δ 7.43 (d, *J* = 2.5 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.34 (d, *J* = 2.5 Hz, 1H), 5.93 (d, *J* = 2.4 Hz, 1H), 1.23 (s, 9H), 1.13 (s, 9H), 0.98 (s, 9H); <sup>13</sup>C NMR (*T* = 278 K) δ 203.8 (s), 173.3 (s), 157.3 (s), 144.4 (s), 141.5 (s, overlapping a signal of 1b), 140.4 (d), 138.1 (s), 135.9 (d), 135.8 (s), 132.7

(d), 126.6 (d), 79.3 (s), 42.4 (s), 34.8 (s), 34.3 (s), 29.1 (q, overlapping a signal of 10i), 28.5 (q), 24.8 (q). During overnight standing of the solution monitored by NMR on ambient temperature, besides 10% decomposition of 10i, *ortho* adduct 12b transformed into *o*-indophenol 14a with formation of 2-methylpropene (13), confirmed by adding it to the recorded solution. **2,6-Dichloro-4-[(3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]imino]-2,5-cyclohexadien-1-*n*** (14a):  $^1\text{H}$  NMR  $\delta$  7.71 (d,  $J$  = 2.5 Hz, 1H), 7.57 (d,  $J$  = 2.5 Hz, 1H), 7.40 (d,  $J$  = 2.2 Hz, 1H, overlapping a signal of 10i), 6.71 (d,  $J$  = 2.2 Hz, 1H), 1.42 (s, 9H), 1.31 (s, 9H);  $^{13}\text{C}$  NMR ( $T$  = 278 K)  $\delta$  173.4 (s), 151.2 (s), 150.3 (s), 142.4 (s), 139.3 (s), 138.9 (d), 136.2 (s), 136.1 (s), 135.2 (s), 128.2 (d), 126.8 (d), 116.5 (d), 34.9 (s), 34.3 (s), 31.6 (q), 29.1 (q, overlapping a signal of 10i). 13:  $^1\text{H}$  NMR ( $T$  = 278 K)  $\delta$  4.65 (septet,  $J$  = 1.1 Hz, 2H), 1.72 (t,  $J$  = 1.1 Hz, 6H);  $^{13}\text{C}$  NMR ( $T$  = 278 K)  $\delta$  142.7 (s), 110.6 (t), 24.2 (q). *o*-Indophenol 14a cyclized into 11c during PTLC (silica, chloroform). After PTLC, red 11c was eluted from the silica with chloroform, dissolved in hexane (40 mL), washed with NaOH (1 M, 4  $\times$  40 mL) and water (2  $\times$  40 mL), and then evaporated. 11c:  $^1\text{H}$  (CDCl<sub>3</sub>)  $\delta$  7.75 (d,  $J$  = 2.4 Hz, 1H), 7.73 (s, 1H), 7.71 (d,  $J$  = 2.4 Hz, 1H), 1.58 (s, 9H), 1.40 (s, 9H);  $^{13}\text{C}$  NMR (relaxation delay\* was 15 s)  $\delta$  172.4 (s), 149.1 (s), 144.9 (s), 144.6 (s), 140.1 (s), 139.9 (s), 137.6 (s), 133.6 (s), 130.6 (d), 129.6 (d), 125.5 (d), 112.2\* (s), 35.2 (s), 35.0 (s), 31.3 (q), 29.6 (q). If oxygen was not removed from the solvents applied in the reaction, 15 and 16 were also formed besides 10i and 12b (10i:12b:15:16  $\approx$  5:3:2:1 by  $^1\text{H}$  NMR). 15:  $^1\text{H}$  NMR  $\delta$  6.72 (s, 4H). 16:  $^1\text{H}$  NMR  $\delta$  6.86 (d,  $J$  = 2.7 Hz, 1H), 6.84 (d,  $J$  = 2.5 Hz, 1H), 6.68 (d,  $J$  = 2.7 Hz, 1H), 6.11 (d,  $J$  = 2.5 Hz, 1H). (Compounds 15 and 16 were also prepared by a different route<sup>64</sup>).

**Reaction of 2,6-Dimethyl-4-*tert*-butylphenol (2s) with 1b.** The same procedure as described for the reaction of 2f and 1b was applied using a solution of 1b (32 mg, 0.15 mmol) in acetonitrile (15 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6  $\times$  10<sup>-3</sup> M), and a solution of 2s (9 mg, 0.05 mmol) in acetonitrile (5 mL) with 15 min reaction time. 12a rapidly decomposes; thus, the  $^1\text{H}$  NMR measurement has to be carried out immediately after processing. Assignment of 3b: see under the reaction of 2c and 1b (3b:12a  $\approx$  1:2 by  $^1\text{H}$  NMR). **2,6-Dichloro-4-[(1,5-dimethyl-3-(1,1-dimethylethyl)-2,4-cyclohexadienyl]imino]-2,5-cyclohexadien-1-one** (12a):  $^1\text{H}$  NMR  $\delta$  7.42 (d,  $J$  = 2.5 Hz, 1H), 7.14 (sextet,  $J$  = 2.4, 1.4 Hz, 1H), 6.37 (d,  $J$  = 2.5 Hz, 1H), 6.02 (d,  $J$  = 2.4 Hz, 1H), 1.99 (d,  $J$  = 1.4 Hz, 3H), 1.72 (s, 3H), 1.16 (s, 9H).

**Reaction of 4-*tert*-Butylphenol (2r) with 1b.** The same procedure as described for the reaction of 2j and 1b was applied using a solution of 1b (63 mg, 0.3 mmol) in acetonitrile (15 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6  $\times$  10<sup>-3</sup> M), and a solution of 2r (340 mg, 2.25 mmol) in acetonitrile (15 mL) with 60 min reaction time but without adding TCE. The residue obtained on evaporation was dissolved in hexane (40 mL) and extracted first with NaOH (1 M, 2  $\times$  30 mL) and then with water (2  $\times$  20 mL). Compounds 11a and 11d were separated by column chromatography (silica, benzene). The fraction containing 11a was rechromatographed (1:1 benzene/chloroform to remove the residual 2r). 3f was isolated from the carbonate solution by neutralization and extraction with dichloromethane and then purification by column chromatography applying first benzene and then 9:1 benzene/ethanol as eluent to remove 2r (3f:11a:11d  $\approx$  10:1:1). 11a:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  7.87 (d,  $J$  = 2.3 Hz, 1H), 7.72 (s, 1H), 7.72 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 7.47 (d,  $J$  = 8.7 Hz, 1H), 1.41 (s, 9H);  $^{13}\text{C}$  NMR  $\delta$  172.5 (s), 150.2 (s), 145.7 (s), 145.1 (s), 141.4 (s), 139.9 (s), 133.1 (s), 131.7 (d), 131.0 (d), 127.1 (d), 116.0 (d), 112.9 (s), 34.8 (s), 31.3 (q). 11d:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  7.89 (d,  $J$  = 2.4 Hz, 1H), 7.77 (s, 1H), 7.70 (dd,  $J$  = 8.7, 2.4 Hz, 1H), 7.67 (d,  $J$  = 2.5 Hz, 1H), 7.38 (d,  $J$  = 8.7 Hz, 1H), 6.89 (d,  $J$  = 2.5 Hz, 1H), 1.40 (s, 9H);  $^{13}\text{C}$  NMR  $\delta$  173.3 (s), 170.2 (s), 159.0 (s), 150.2 (s), 146.0 (s), 141.6 (s), 139.3 (s), 138.6 (d), 138.5 (s), 138.2 (s), 137.4 (s), 133.6 (s), 131.9 (d), 131.1 (d), 127.4 (d), 127.2 (d), 126.0 (s), 116.0 (d), 34.8 (s), 31.2 (q).

**Reaction of 1b with Sodium Phenolate. Method a:** After adding a solution of sodium salt of 2a (24 mg, 0.21 mmol), dissolved by warming and cooling, in DMSO-*d*<sub>6</sub> (1.2 mL) to a solution of 1b (52 mg, 0.25 mmol) in DMSO-*d*<sub>6</sub> (0.3 mL), the  $^1\text{H}$ -NMR spectra of this mixture was recorded immediately. 18a:  $^1\text{H}$  NMR  $\delta$  7.77 (d,  $J$  = 2.5 Hz, 1H), 7.56 (t,  $J$  = 8.1 Hz, 2H), 7.38 (t,  $J$  = 8.1 Hz, 1H), 7.29 (d,  $J$  = 8.1 Hz, 2H), 6.50 (d,  $J$  = 2.5 Hz, 1H). Besides 18a, indophenol 3f was also formed but their ratio was determined by chromatography because signals of 3f were broad and flat. After recording the  $^1\text{H}$  NMR spectra, to this solution was added HCl solution (30 mL, 10<sup>-4</sup> M) and then extracted with dichloromethane (50 mL, 20 mL). The organic solution was washed with water (2  $\times$  30 mL), dried, and evaporated. 18a and 3f were separated by column chromatography. Firstly 18a was obtained (3:2 dichloromethane/hexane, *R*<sub>f</sub> 0.55) and then 3f was eluted (dichloromethane, *R*<sub>f</sub> 0.25). The ratio of 18a:3f was 96:4. **Method b:** To a solution of the sodium salt of 2a (6 mg, 0.05 mmol) and 18-crown-6 (28 mg, 0.1 mmol) in acid-free chloroform-*d* (0.3 mL) was poured a solution of 1b (13 mg, 0.06 mmol) in chloroform-*d* (0.3 mL), and the  $^1\text{H}$  NMR spectra of this solution was recorded immediately. 3f:  $^1\text{H}$  NMR  $\delta$  7.33 (d,  $J$  = 9.9 Hz, 2H), 7.27 (s, 2H) 6.57 (d,  $J$  = 9.9 Hz, 2H).

**Preparation of *O*-Phenyl-2,6-dichloroquinone 4-Oxime (19b).** *O*-Phenylhydroxylamine hydrochloride<sup>65</sup> (1240 mg, 8.5 mmol) was added to a solution of sodium ethoxide (0.04 M, 21.3 mL) at -30 °C. Sodium chloride was filtered off and washed with cold ethanol (5 mL). This solution was added to a hot solution of 2,6-dichloroquinone (1504 mg, 8.5 mmol) in ethanol (20 mL). Thereafter, HCl-ethanol (1 mL, 10%) was added dropwise to the solution, which initiated the precipitation of the product. The mixture was cooled and filtered and the product was recrystallized from ethanol (320 mg yellow needles, sensitive to light, mp 167–168 °C). 19b:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  8.07 (d,  $J$  = 2.5 Hz, 1H), 7.53 (d,  $J$  = 2.5 Hz, 1H), 7.39 (t,  $J$  = 7.8 Hz, 2H), 7.30 (d,  $J$  = 7.8 Hz, 2H), 7.18 (t,  $J$  = 7.8 Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  173.2 (s), 158.3 (s), 148.3 (s), 139.0 (s), 135.1 (s), 133.6 (d), 129.6 (d), 124.8 (d), 122.1 (d), 114.9 (d). **Anal.** Calcd for C<sub>12</sub>H<sub>7</sub>NO<sub>2</sub>Cl<sub>2</sub>: C, 53.76; H, 2.63; N, 5.22; Cl, 26.45. Found: C, 53.67; H, 2.56; N, 5.11; Cl, 26.39.

**Photoizomerization of 19b.** A mixture of a solution of 19b (15 mg, 0.06 mmol) in acetonitrile (70 mL) and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (125 mL, 0.01 M) was irradiated for 20 min using a 125 W Philips HPK BA 15D immersion lamp with an S-shaped vessel. To this mixture was added water (100 mL) and then neutralized with HCl (3.3 mL, 1 M) and extracted with dichloromethane (100 mL + 50 mL). The organic layer was washed with water, dried, and evaporated at reduced pressure. According to the  $^1\text{H}$  NMR spectra of this residue in CDCl<sub>3</sub>, only 2a, 3f, and 11b were observed. The ratio of 2a:3f:11b was 1.6:2:1. After recording the NMR spectra, dichloromethane (25 mL) was added, washed with NaOH (3  $\times$  25 mL, 0.1 M) and water (2  $\times$  20 mL), dried, and then evaporated. 11b:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  7.89 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 7.73 (s, 1H), 7.66 (ddd,  $J$  = 8.6, 8.4, 1.5 Hz, 1H), 7.54 (dd,  $J$  = 8.4, 1.4 Hz, 1H), 7.47 (ddd,  $J$  = 8.6, 7.9, 1.4 Hz, 1H).

**Reaction of 3,5-Di-*tert*-butylphenol (2t) with 1g.** The same procedure as described for the reaction of 2j and 1b was applied using a solution of 1g<sup>66</sup> (42 mg, 0.16 mmol) in acetonitrile (25 mL), a solution of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (225 mL, 6  $\times$  10<sup>-3</sup> M), and a solution of 2t (124 mg, 0.6 mmol) in acetonitrile (10 mL) with 70 min reaction time, but the hexane layer was washed with NaOH (0.1 M, 3  $\times$  100 mL) before washing with water. The mixture of 11e and 11f (their ratio was 3:5) was purified by column chromatography (95:5 benzene/acetone, silica). 11e:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  7.42 (d,  $J$  = 2.0 Hz, 1H), 7.22 (d,  $J$  = 2.0 Hz, 1H), 7.06 (d,  $J$  = 2.0 Hz, 1H), 6.26 (d,  $J$  = 2.0 Hz, 1H), 1.61 (s, 9H), 1.38 (s, 9H). 11f:  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  7.80 (d,  $J$  = 2.4 Hz, 1H), 7.64 (d,  $J$  = 2.4 Hz, 1H), 7.10 (d,  $J$  = 2.0 Hz, 1H), 6.35 (d,  $J$  = 2.0 Hz, 1H), 1.49 (s, 9H), 1.39 (s, 9H). The presence of 11f prepared by a different way, by the reaction of 2al and 1g, was verified by adding it to the measured solution.

(65) Nicholson, J. S.; Peak, D. A. *Chem. Ind.* 1962, 1244.

(66) 1g was contaminated by 10% of 2,6-dichlorobenzoquinone.

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**Supplementary Material Available:** Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of all compounds and the Job plots of the Gibbs reaction of 1b with 2b, 2c and 2k (72 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.